

Indicator: Nitrate, Phosphorus, and Pesticides in Streams in Agricultural Watersheds (040)

Nitrogen is a critical plant nutrient, and most nitrogen is used and reused by plants within an ecosystem (Vitousek, et al., 2002). Thus, in undisturbed ecosystems, minimal “leakage” occurs into either surface runoff or groundwater, and concentrations are very low. However, when nitrogen is applied to the land in amounts greater than can be incorporated into crops or lost to the atmosphere through volatilization or denitrification, nitrogen concentrations in streams can increase. The major sources of excess nitrogen are fertilizer and animal waste; other sources include onsite septic systems, sewage treatment plants, and atmospheric deposition. In drinking water, concentrations of nitrate above the federal standard of 10 mg/L may pose a risk of methemoglobinemia, a condition that interferes with oxygen transport in the blood of infants (EPA, 2004). Excess nitrate has not been shown to harm aquatic life in the stream directly, but increased nitrogen/nutrients may result in overgrowth of algae which can decrease the dissolved oxygen content of the water, thereby harming or killing fish and other aquatic species (U.S. EPA, 2005a). In addition, excess nitrate can damage coastal ecosystems downstream, as discussed further in the indicator “Nitrogen and Phosphorus Discharge from Large Rivers.”

Phosphorus is an essential nutrient for all life forms, but at high concentrations the most biologically active form of phosphorus can cause water quality problems by overstimulating the growth of algae. In addition to being visually unappealing and causing tastes and odors in water supplies, excess algal growth can contribute to the loss of oxygen needed by fish and other animals. Elevated levels of phosphorus in streams can result from fertilizer use, animal wastes and wastewater, and some detergents.

More than one billion pounds of pesticides are used in the United States each year to control weeds, insects, and other organisms that threaten or undermine human activities (Aspelin, 2003). About 80% of the total is used for agricultural purposes. Although pesticide use has resulted in increased crop production and other benefits, pesticide contamination of streams, rivers, lakes, reservoirs, coastal areas, and groundwater may cause unintended adverse effects on aquatic life, recreation, drinking water, irrigation, and other uses. Water also is one of the primary pathways by which pesticides are transported from their application areas to other parts of the environment (USGS, 2000).

This indicator is based on stream water samples collected between 1992 and 2001 from watersheds where agriculture represents the predominant land use, as part of the U.S. Geological Survey’s National Water Quality Assessment (NAWQA) Program. Nitrate and phosphorus data are based on 12 to 25 samples collected annually at stream sites draining 115 watersheds in 49 major river basins across the conterminous United States. At each stream site, samples were collected at multiple times each year over a 1-to-3-year period. The indicator is based on a flow-weighted annual average of the samples. A related indicator reports the concentrations of nitrate and pesticides in groundwater in agricultural watersheds (Indicator “Nitrate and Pesticides in Groundwater in Agricultural Watersheds”).

For nitrate, the indicator reports the percent of streams with average concentrations in one of four ranges: less than 2 parts per million (mg/L); 2-6 mg/L; 6-10 mg/L; and 10 mg/L or more. The highest level (10 mg/L) represents the Maximum Contaminant Level (MCL) for nitrate allowed in finished drinking water in the U.S. (U.S.EPA, 2005b), but because people are unlikely to drink untreated stream water, this concentration should be viewed as a reference level, and not necessarily as a health risk to consumers. There is no comparable aquatic health guideline for nitrate because nitrate does not represent a direct threat to organisms living in the stream.

Phosphorus concentrations are reported in four ranges: less than 0.1 mg/L, 0.1-0.3 mg/L, 0.3-0.5 mg/L, and 0.5 mg/L or more. There is currently no national water quality criterion to protect surface waters because the effects of phosphorus vary by region and are dependent on physical factors such as the size,

hydrology, and depth of rivers and lakes. In general, levels above 0.1 mg/L have been associated with risks of nuisance growths of algae.

Pesticide data reflect conditions in 83 agricultural watersheds where NAWQA collected 10 to 49 stream water samples per year and analyzed for 76 different pesticides and 7 pesticide degradation products. Together, the analyzed compounds account for approximately 75% of the total amount of agricultural pesticides applied annually in the United States by weight (USGS, 1999). This indicator reports the number of sites where the annual time-weighted average concentration of one or more of these pesticides or their degradation products exceeds standards for aquatic or human health.

Three types of U.S. EPA human health-related standards and guidelines were used as reference levels for pesticide concentrations: Maximum Contaminant Levels (MCLs), Risk-Specific Dose (RSD), and Lifetime Health Advisory (HA-L) (U.S. EPA 2000, 2001). In all three cases, the standard and guideline levels are concentrations that pertain to lifetime exposure through drinking water (RSDs relate to potential carcinogens and HA-Ls relate to non-carcinogenic adverse health effects). More detail on these types of benchmarks, their derivation, and their underlying assumptions is provided in Nowell and Resek (1994). If a chemical had multiple benchmarks, the MCL was used if available; otherwise, the lower of the RSD (at 1 in 100,000 cancer risk) and HA-L values was selected. An exceedance was identified if a yearly, time-weighted mean concentration exceeded the relevant standard or guideline (Heinz Center, 2002).

The three types of freshwater aquatic-life guidelines used as reference levels for pesticides in this indicator are U.S. EPA chronic water-quality criteria for protection of aquatic organisms, Canadian water quality guidelines, and International Joint Commission (IJC) Great Lakes water-quality objectives (summarized at <http://ca.water.usgs.gov/pnsp/source/>). The U.S. EPA chronic water-quality criterion for protection of aquatic organisms is the estimated highest concentration of a constituent that aquatic organisms can be exposed to for a 4-day period, once every 3 years, without deleterious effects; the IJC and Canadian water-quality guidelines specify maximum concentrations that should not be exceeded at any time. If no U.S. EPA criterion existed for a given constituent, then Canadian water-quality guidelines were used, if available. The older IJC Great Lakes water-quality objectives were used only if neither U.S. EPA criteria nor Canadian guidelines were available. A concentration exceeding the aquatic-life guidelines in any single surface water sample was counted as an exceedance of the guideline.

What the Data Show

NAWQA data indicate that during the 1992-2001 period:

- Average flow-weighted nitrate concentrations were above 2 mg/L in about half of the stream sites where agriculture is the primary land use in the watershed (Figure 040-1). About 12% of stream sites had nitrate concentrations above the federal drinking water MCL of 10 mg/L.
- More than three-fourths of agricultural streams had average annual flow-weighted concentrations of phosphorus above 0.1 mg/L while nearly 15% had phosphorus concentrations above 0.5 mg/L (Figure 040-2).
- The annual average time-weighted concentration of at least one pesticide exceeded aquatic life guidelines in more than 75% of the streams sampled (Figure 040-3). Human health criteria for one or more pesticides were exceeded in 7.2% of streams.

At least one pesticide was present at detectable levels throughout the year in all monitored streams (Martin et al., 2003). NAWQA data indicate that, in agricultural streams, pesticides most often occur in mixtures (i.e., more than one compound is present in the sample). The human health and environmental impacts of pesticide contamination, particularly when the pesticides occur as mixtures, are not well understood.

Indicator Limitations

- These data represent conditions in streams draining agricultural watersheds in the 49 major river basins or study units sampled by the NAWQA program in the conterminous U.S. While they were subjectively chosen to be representative of agricultural watersheds across the United States, they are the result of a targeted sample design, and may not be an accurate reflection of the distribution of concentrations in all streams in agricultural watersheds in the U.S.
- Drinking water treatment can significantly reduce concentrations of nitrate and many pesticides. Thus, the levels of contaminants reported in this indicator are not necessarily representative of the exposures to people when these waters are used as public drinking water supplies.
- U.S. and Canadian aquatic life criteria and guidelines reflect exposures of 1-4 days; the use of annual flow- or time-weighted averages may mask 1-4 day concentrations that exceed guidelines in any particular stream. Aquatic life guidelines do not currently exist for 64% (51 of 80) of the pesticides and pesticide degradation products analyzed, while drinking water standards or guidelines do not exist for 44% (35 of 80). Current standards and guidelines do not account for mixtures of pesticide chemicals and seasonal pulses of high concentrations. Possible pesticide effects on reproductive, nervous, and immune systems, as well as on chemically sensitive individuals, are not yet well understood.
- This indicator does not provide information on the degree to which pesticide concentrations exceed or fall below guidelines.

Data Sources

Data for this indicator were collected and compiled by the U.S. Geological Survey's National Water Quality Assessment (NAWQA) Program. More information on this program can be found at <http://water.usgs.gov/nawqa/>.

References

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Martin, J.D., Crawford, C.G., and Larson, S.J. 2003. Pesticides in Streams: Summary Statistics; Preliminary Results from Cycle I of the National Water Quality Assessment Program (NAWQA), 1992-2001. U.S. Geological Survey. February 19, 2003. http://ca.water.usgs.gov/pnsp/pestsw/Pest-SW_2001_Text.html.

Nowell, L.H., and Resek, E.A. 1994. National standards and guidelines for pesticides in water, sediment, and aquatic organisms: Application to water-quality assessments: Rev. Environ. Contam. Toxicol. v. 140, pp. 1-164.

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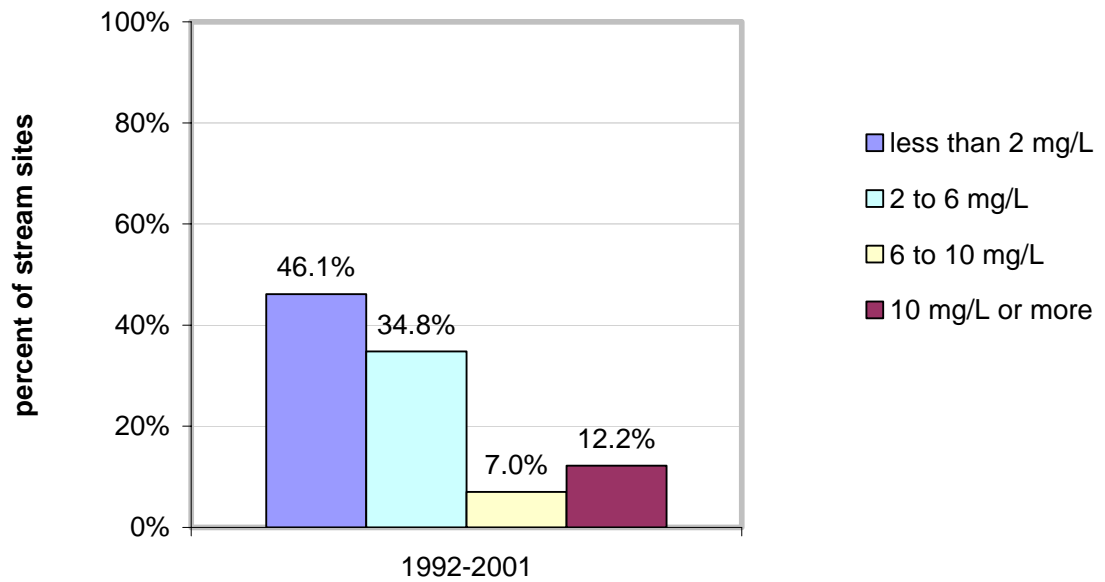
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<http://ca.water.usgs.gov/pnsp/rep/fs09200/>

Vitousek, P., Mooney, H., Olander, L., and Allison, S. 2002. Nitrogen and nature. *Ambio* 31: 97-101.

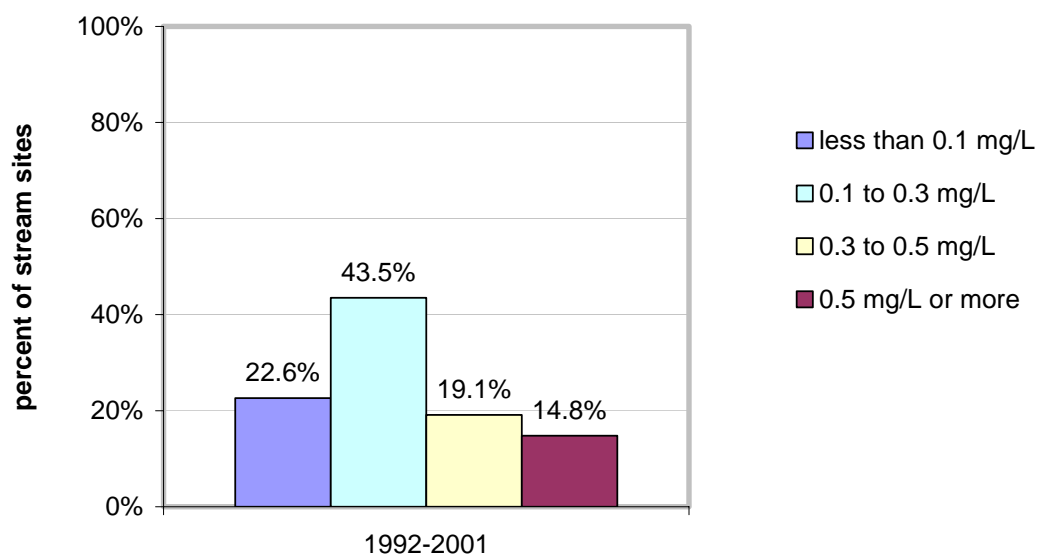
Graphics

Figure 040-1. Nitrate in streams in 115 agricultural watersheds, 1992-2001

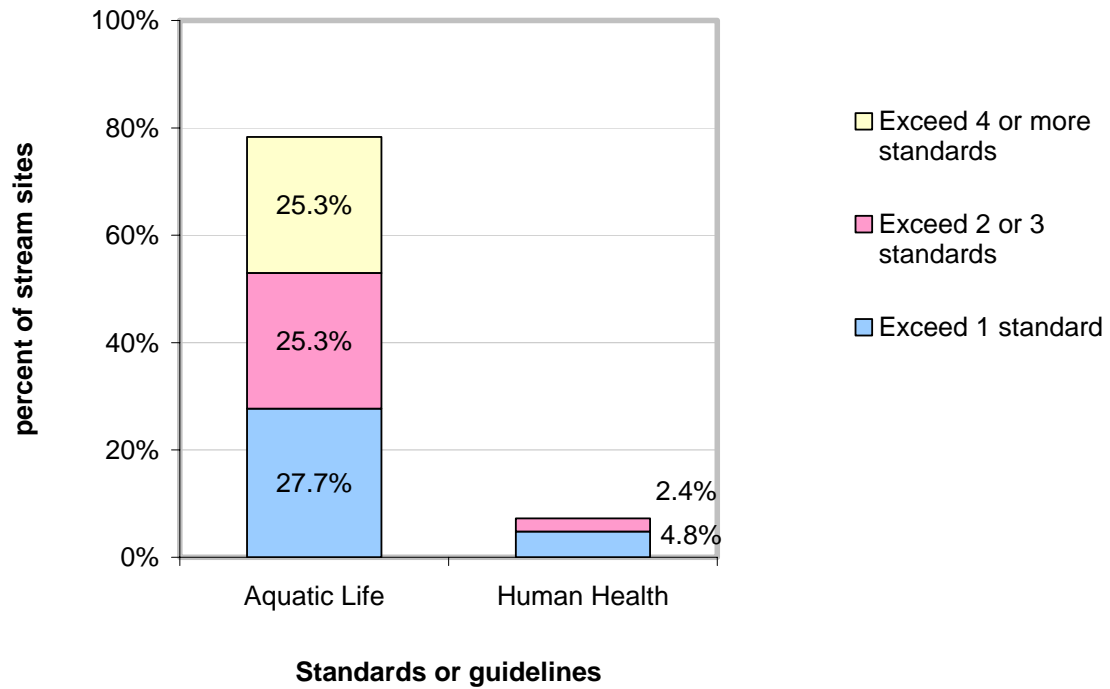


EPA's drinking water standard is 10 mg/L (Maximum Contaminant Level, or MCL).

Figure 040-2. Total phosphorus in streams in 115 agricultural watersheds, 1992-2001



**Figure 040-3. Pesticides in streams in agricultural watersheds,
1992-2001**



R.O.E. Indicator QA/QC

Data Set Name: NITRATE, PHOSPHORUS, AND PESTICIDES IN STREAMS IN AGRICULTURAL WATERSHEDS

Indicator Number: 040 (89863)

Data Set Source: U.S. Geologic Survey

Data Collection Date: Irregular: 1993-1998

Data Collection Frequency: 1wk. - 1yr.

Data Set Description: Nitrate, Phosphorus, and Pesticides in Streams in Agricultural Watersheds

Primary ROE Question: What are the trends in extent and condition of fresh surface waters in the United States?

Question/Response

T1Q1 Are the physical, chemical, or biological measurements upon which this indicator is based widely accepted as scientifically and technically valid?

Field and laboratory methods are documented in official publications of the U.S. Geological Survey (USGS), which oversees the National Water Quality Assessment (NAWQA) Program that collected and analyzed the data for this indicator (full publication citations may be found in T3Q1). Field sampling follows established protocols that dictate how a sample is collected, depth-and-width integrated (to represent the full cross-section of the stream), and preserved (Shelton, 1994). These protocols include criteria for collection equipment, how the equipment is cleaned, and how samples are filtered to remove suspended particulate matter (<http://ca.water.usgs.gov/pnsp/pestsw/>). Laboratory analysis employs a variety of methods, which are described and cited in T3Q1. For each chemical, NAWQA uses the laboratory method that has been shown to be most sensitive and accurate. Each chemical/method has its own unique detection limit, but for the purposes of this survey, all relevant detection limits have been documented appropriately (<http://ca.water.usgs.gov/pnsp/anstrat/>).

T1Q2 Is the sampling design and/or monitoring plan used to collect the data over time and space based on sound scientific principles?

This indicator is based on data collected by USGS's NAWQA program. NAWQA's overall sample design represents a comprehensive effort to assess the nation's water quality through study units across the lower 48 states, which were chosen to be broadly representative of various land uses. Gilliom et al. (1995) provides an official description of sample design (full citation in T3Q3). The data for this indicator were collected between 1992 and 2001, a period that covers three full NAWQA sampling cycles and a total of 49 NAWQA study units. Within these 49 study units were several watersheds in which agriculture was considered a significant land use, according to a standard set of criteria described in Gilliom and Thelin (1997) (full citation in T3Q3). Samples from 115 agricultural watersheds were analyzed for nitrate and phosphorus, while only 83 watersheds were screened for pesticides, due to the higher cost and complication of laboratory analysis for 83 different chemicals. Nonetheless, because of NAWQA's scientific sampling design, results are considered to be fairly representative of conditions in agricultural watersheds nationwide.

T1Q3 Is the conceptual model used to transform these measurements into an indicator widely accepted as a scientifically sound representation of the phenomenon it indicates?

To determine whether the concentrations of nitrate and phosphorus in a stream exceeded water quality standards, NAWQA calculated a flow weighted mean concentration. This type of calculation uses a regression model to transform non-daily measurements into a mean value that accounts for day-to-day variability in streamflow (volume) over the course of a given year. USGS commonly calculates a flow weighted mean when the concentration of a given constituent in this case, nitrate or phosphorus may be correlated with streamflow (i.e., total load is an issue). NAWQA has documented the nitrate and phosphorus regression model for this indicator at <http://water.usgs.gov/nawqa/nutrients/datasets/nutconc2000>. According to this description, NAWQA calibrated the regression model for this indicator using 1 to 2 years of daily streamflow data from USGS

gages located at or near each of the water quality sampling sites. These gages are part of a network of thousands of USGS stream gages located across the U.S. A single gage may measure volumetric discharge directly using a current meter, or it may measure indirectly using calculations that can be performed on measurements of stream depth (a unique rating curve for each stream, relating volume to stream height). Collection of streamflow data follows long-standing USGS protocols. For a discussion and validation of these protocols, consult the following USGS online references: Depth (stage) gauging: <http://water.usgs.gov/pubs/twri/twri3-A6/> and <http://water.usgs.gov/pubs/twri/twri3a7/>. Conversion of depth to discharge: <http://water.usgs.gov/pubs/twri/twri3-a1/> and <http://water.usgs.gov/pubs/twri/twri3-a10/>. Direct measurement of discharge: <http://water.usgs.gov/pubs/twri/twri3a8/>. NAWQA calculated pesticide concentrations from each sampling site in the form of a time weighted mean. This step is necessary to generate a true average value, as samples were not necessarily collected at even intervals during the year, and taking a simple arithmetic mean would give disproportionate weight to samples taken during periods of high sampling frequency. Because NAWQA timed a significant portion of sampling events to occur during periods of heaviest pesticide application (in order to keep closer tabs on the higher end of potential exposures), a simple arithmetic mean would likely overstate mean annual concentrations. The time weighted mean approach is therefore more appropriate for this indicator. This approach is fully documented at <http://ca.water.usgs.gov/pnsp/rep/wrir984222/methods.html#data>. Standards and guidelines for human and ecological health are documented in T2Q3. All have been determined scientifically by the appropriate government agencies.

T2Q1 To what extent is the indicator sampling design and monitoring plan appropriate for answering the relevant question in the ROE?

Overall, the spatial, temporal, and chemical coverage of this indicator are appropriate for reporting on the national issue of chemical contamination of streams in agricultural areas. This indicator uses a limited number of watersheds as a basis for generating an overall national indicator. However, the NAWQA program was specifically designed with this in mind, as the program intentionally sought to sample streams draining representative watersheds of each of the major land-use types, sometimes referred to as indicator sites. NAWQA study units are spread across the lower 48 states, as shown by the map on NAWQA's website (<http://water.usgs.gov/nawqa/>). Beginning in 1991, NAWQA set out to examine 51 study areas. The subsequent 9-year period was divided into three-year cycles, with approximately one-third of the study units intensely sampled during each cycle. This indicator reports data from 49 study units that were sampled intensely during these three cycles, between 1992 and 2001. Within each study unit, major streams were sampled 10-49 times per year over the period of intense monitoring, and less frequently in other years. For this indicator, the Heinz Center only used NAWQA data from the 1-3 years of most intense monitoring for each site. This indicator reports chemical concentrations in streams draining watersheds where agriculture was considered to represent a primary land use. However, NAWQA also sampled several forest and urban streams in order to provide some useful context for the agricultural data. Nutrient and pesticide data are not completely comparable, as nitrate and phosphorus were measured in 115 watersheds, and pesticides screened in only 83 (due to the greater cost and complication of laboratory analysis for a suite of 83 pesticide chemicals). However, both datasets were designed to be reflective of conditions nationwide, and both also reflect smoothing procedures that were used to transform a limited number of measurements (nitrate/phosphorus: 12-25 measurements; pesticides: 10-49) into long-term mean values. For nitrate and phosphorus, this step required a flow weighted regression approach that considers how concentrations vary with streamflow; for pesticides, it required a time weighted mean approach to reduce any bias toward periods of more frequent sampling (although averages may still only represent five months of frequent sampling, not full annual values). Averaging is appropriate and important for both nutrients and pesticides, as this indicator seeks to evaluate chemical concentrations in the context of long-term exposure thresholds for human and ecological health. In each case, NAWQA considered the most recent and relevant health criteria available. In terms of chemicals, this indicator covers a broad range of compounds that may be present as a result of agricultural applications. Nitrate, though it occurs naturally, may also be found in elevated levels due to the presence of runoff from fertilizer as well as human and animal waste. Runoff from fertilizer and animal wastes can also lead to elevated levels of phosphorus. The 76 pesticides and 7 pesticide degradation products screened for this indicator represent approximately 75% of the total agricultural pesticide application in the U.S. (NAWQA: <http://ca.water.usgs.gov/pnsp/anstrat/>). All are

chemicals whose presence may be of concern to humans who use stream water as their domestic water supply, particularly if it is untreated.

T2Q2 To what extent does the sampling design represent sensitive populations or ecosystems?

This broad national indicator is not specifically designed to target sensitive populations or ecosystems. It may be relevant to sensitive populations, however, to the extent that certain endangered species may be particularly sensitive to chemical contaminants.

T2Q3 Are there established reference points, thresholds or ranges of values for this indicator that unambiguously reflect the state of the environment?

This indicator does not provide a historical or undisturbed baseline against which recent data may be compared. However, for many of the chemicals screened, EPA and other government agencies have established reference concentrations for human and/or ecological/aquatic health. The reference threshold for nitrate is 10 mg/L, which is EPA's Maximum Contaminant Level (MCL). Phosphorus thresholds vary by state or region, in part because the effects of phosphorus are dependent on physical factors such as the size, hydrology, and depth of rivers and lakes. In general, levels above 0.1 mg/L have been associated with risks of nuisance growths of algae. Reference thresholds for pesticides are listed at <http://ca.water.usgs.gov/pnsp/anstrat/> and sources of these values are listed at <http://ca.water.usgs.gov/pnsp/source/>. For some pesticide-related contaminants, reference values have not yet been established.

T3Q1 What documentation clearly and completely describes the underlying sampling and analytical procedures used?

All NAWQA sampling procedures are documented in official USGS reports (full citations appear below). Shelton (1994) describes field sampling protocols, including depth and width integrating techniques that ensure that stream samples represent the entire cross-section of the stream. Shelton (1994) also discusses methods of sample preservation. Laboratory methods are fully documented by USGS. NAWQA measured nitrate concentrations using procedures described in Fishman (1993); analytical procedures for total phosphorus are described in Patton and Truitt (1992). Pesticide concentrations were measured using two primary methods: gas chromatography/mass spectrometry (GC/MS) (Zaugg et al., 1995) and high-performance liquid chromatography (HPLC) (Werner et al., 1996). The website <http://ca.water.usgs.gov/pnsp/anstrat/> provides a list of the 76 pesticides and 7 related degradation products that NAWQA screened, along with the specific laboratory method used for each (see Table 2 on this website). This website also lists detection limits, which are compound-specific. Because nitrate and phosphorus concentrations typically vary with streamflow (volume), NAWQA calculated a flow-weighted mean concentration using a regression model. The model for this indicator is documented at <http://water.usgs.gov/nawqa/nutrients/datasets/nutconc2000>. NAWQA calibrated this model using 1 to 2 years of daily streamflow data from USGS gages located at each of the water quality sampling sites (or nearby, when the sampling site could not be located directly at a stream gage). Streamflow data may be obtained from USGS's database, <http://waterdata.usgs.gov/nwis/sw>, and methods of streamflow data collection are documented in the following USGS online references: Depth (stage) gauging: <http://water.usgs.gov/pubs/twri/twri3-A6/> and <http://water.usgs.gov/pubs/twri/twri3a7/>. Conversion of depth to discharge: <http://water.usgs.gov/pubs/twri/twri3-a1/> and <http://water.usgs.gov/pubs/twri/twri3-a10/>. Direct measurement of discharge: <http://water.usgs.gov/pubs/twri/twri3a8/>. For pesticides, NAWQA used a time weighted mean approach to ensure that the annual average values reported were not biased towards periods of more frequent sampling (since sampling was not always done at regular intervals). NAWQA has fully documented this approach at <http://ca.water.usgs.gov/pnsp/rep/wrir984222/methods.html#data>. This indicator reports an exceedance if any single measurement exceeds an aquatic health guideline, or if the time weighted mean exceeds the relevant human health guideline. Fishman, M.J. 1993. Methods of analysis by the U.S. Geological Survey National Water-Quality Laboratory--Determination of inorganic and organic constituents in water and fluvial sediments. U.S. Geological Survey Open-File Report 93-125. Patton, C.J., and Truitt, E.P. 1992. Methods of analysis by the U.S. Geological Survey National Water Quality

Laboratory--Determination of total phosphorus by a Kjeldahl digestion method and an automated colorimetric finish that includes dialysis: U.S. Geological Survey Open-File Report 92-146, 39 p. Method ID: I-4610-91. Shelton, L.R. 1994. Field guide for collecting and processing stream water samples for the National Water-Quality Assessment Program. U.S. Geological Survey Open-File Report 94-455. Werner, S.L., Burkhardt, M.R., and DeRousseau, S.N. 1996. Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory: Determination of pesticides in water by Carbopak-B solid-phase extraction and high-performance liquid chromatography: U.S. Geological Survey Open-File Report 96-216, Denver, Colorado, 42 pp. Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M. 1995. Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory-Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S.

T3Q2 Is the complete data set accessible, including metadata, data-dictionaries and embedded definitions or are there confidentiality issues that may limit accessibility to the complete data set?

Water quality data collected by NAWQA may be accessed through the NAWQA database, http://infotrek.er.usgs.gov/servlet/page?_pageid=543&_dad=portal30&_schema=PORTAL30. These data may also be accessed through USGS's general water quality database, located at <http://waterdata.usgs.gov/nwis/qw>. Streamflow data are available from USGS at <http://waterdata.usgs.gov/nwis/sw>. This indicator depicts a subset of NAWQA data, which have been processed and classified by land-use type. EPA obtained the processed data for this indicator directly from NAWQA. While this data compilation has not been published, NAWQA can provide the data upon request. A similar dataset representing the first two NAWQA cycles (1992-1998) appeared in the Heinz Center's 2002 report, The State of the Nation's Ecosystems. For nitrate and phosphorus concentrations, this dataset may be accessed online at <http://water.usgs.gov/nawqa/nutrients/datasets/nutconc2000/>. This indicator reports data for nitrate plus nitrite, which is often abbreviated as nitrate because concentrations of nitrite are typically small relative to concentrations of nitrate. Phosphorus measurements represent total phosphorus. For pesticide concentrations, the report NAWQA prepared for the Heinz Center is not available online.

T3Q3 Are the descriptions of the study or survey design clear, complete and sufficient to enable the study or survey to be reproduced?

NAWQA and the Heinz Center have provided several references to document the design of the survey upon which this indicator is based. Gilliom et al. (1995) discusses the overall design of the NAWQA program, while Gilliom and Thelin (1997) provides a good description of how watersheds were classified as to land use. NAWQA's report to the Heinz Center (http://water.usgs.gov/nawqa/nutrients/datasets/nutconc2000/sw_nuts_Heinz.xls) includes a list of the 105 locations where nutrient samples were collected for agricultural watersheds during the first two NAWQA cycles. A similar list is not immediately available for pesticide measurement sites, although all watersheds sampled for pesticides are also among those sampled for nutrients. Up-to-date lists may be obtained from NAWQA upon request. NAWQA has published a full list of the pesticides and related degradation products that were screened for this indicator: <http://ca.water.usgs.gov/pnsp/anstrat/>. Gilliom, R.J., W.M. Alley, and M.E. Gurtz. 1995. Design of the National Water-Quality Assessment Program: Occurrence and distribution of water-quality conditions. U.S. Geological Survey Circular 1112. Gilliom, R. J., and G.P. Thelin. 1997. Classification and mapping of agricultural land for National Water-Quality Assessment. U.S. Geological Survey Circular 1131.

T3Q4 To what extent are the procedures for quality assurance and quality control of the data documented and accessible?

Mueller et al. (1997) describes QA/QC procedures for the collection and analysis of stream water quality samples under the NAWQA program. Procedures documented include field blanks and replicates. Mueller, D. K., J.D. Martin, and T.J. Lopes. 1997. Quality-control design for surface water sampling in the National Water-Quality Assessment program. U.S. Geological Survey Open-File Report 97-223. (<http://water.usgs.gov/nawqa/protocols/OFR97-223/index.html>).

T4Q1 Have appropriate statistical methods been used to generalize or portray data beyond the time or spatial locations where measurements were made (e.g., statistical survey inference, no generalization is possible)?

To transform a limited number of water quality samples (10 to 49 annually) into an indicator that characterizes mean concentrations, NAWQA had to employ some degree of spatial and temporal manipulation. Data manipulation procedures are generally well documented and appear to be used appropriately, although the exact specifications of the nutrient regression model are not described in NAWQA's online documentation. Spatially, this indicator requires that a given sample be representative of the entire cross-section of the stream in question, since the measurement should characterize the average condition of stream water in the watershed. NAWQA collected samples with this concern in mind, as described by Shelton (1994) (full citation below). Temporally, this indicator requires that a limited number of daily samples be transformed into a figure that accounts for day-to-day and seasonal variability. For nitrate and phosphorus, the model must account for streamflow, which can affect the overall concentrations. To this end, NAWQA employed a regression model that incorporated daily streamflow data from nearby USGS stream gages. This kind of modeling is a common and appropriate way to generate flow weighted mean values, as described in the documentation cited in T3Q3. For pesticides, NAWQA targeted periods of high use and high runoff for more frequent sampling, but made sure that samples were still collected from the other months of the year. To generate a realistic annual average, NAWQA used a time weighted mean approach, which ensures that periods of high sampling frequency are not over-represented in the final average. Shelton, L.R. 1994, Field guide for collecting and processing stream water samples for the National Water-Quality Assessment Program. U.S. Geological Survey Open-File Report 94-455.

T4Q2 Are uncertainty measurements or estimates available for the indicator and/or the underlying data set?

Uncertainty estimates are not available for the exact subset of data included in this indicator. However, NAWQA has published uncertainty figures for the overall data collection effort, which should be indicative of uncertainty for this indicator. Mueller (1998) specifically discusses nutrient (nitrate and phosphorus) data, while Martin (2002) evaluates uncertainty for pesticide data. Mueller, D.K. 1998. Quality of nutrient data from streams and ground water sampled during 1993-95--National Water-Quality Assessment Program, U.S. Geological Survey Open File Report 98-276. Martin, J.D. 2002. Variability of pesticide detections and concentrations in field replicate water samples collected for the National Water-Quality Assessment Program 1992-97, U.S. Geological Survey Water Resources Investigation Report 01-4178.

T4Q3 Do the uncertainty and variability impact the conclusions that can be inferred from the data and the utility of the indicator?

Because uncertainty varies depending on the chemical and analytical method in question, it is difficult to make a single definitive statement about the impact of uncertainty on this indicator. However, because results are averaged over time and generalized over the entire nation, the summary figures reported by this indicator should be considered reasonably accurate. By incorporating flow- or time-weighted averages, the indicator design also accounts for much of the day-to-day and seasonal variability inherent in measurements of chemicals whose concentrations in stream water are linked in large part to streamflow or to the timing of pesticide application. The use of a time-weighted average for pesticides also accounts for variability in sampling frequency, which is inherent in NAWQA's targeted sampling program. This indicator does not account for year-to-year variability. NAWQA's overall sample design did include sampling streams outside of the 1 to 3 years of most intensive sampling, in order to account for year-to-year variability. However, the indicator was intended only to measure current conditions; as such, it does not include chemical concentrations measured outside of the intensive sampling window. In the future, once additional NAWQA cycles have been completed, this indicator should be able to present information on multi-year trends.

T4Q4 Are there limitations, or gaps in the data that may mislead a user about fundamental trends in the indicator over space or time period for which data are available?

Limitations to this indicator include the following: 1. Although NAWQA measured several different nutrients in water, this indicator is limited to nitrate (actually nitrate plus nitrite) and phosphorus. It does not report concentrations of other forms of nitrogen (e.g., ammonia) that may also result from agricultural

runoff. 2. This indicator is limited to streams. It does not report the condition of lakes and other surface bodies of water. 3. Data for this indicator only represent conditions in 49 NAWQA study areas, each of which typically encompasses a single major river basin. While study units were subjectively chosen to be representative of watersheds across the U.S., they still reflect the results of a targeted sample, not a full survey of all watersheds. Data are also highly aggregated and should only be interpreted as an indication of national patterns. 4. This indicator does not report the extent to which concentrations may be above or below standards for human or ecological health; it just reports whether the standard has been exceeded. It also does not report the extent to which concentrations may exceed other reference values that were not used for this report (e.g., Maximum Contaminant Level Goals (MCLGs) for drinking water). 5. Many chemicals lack an established reference value for human health, aquatic life, or both. There are no established aquatic life standards for nitrate, and no national human or aquatic standards for phosphorus. Of the 76 pesticides screened, only 43 have benchmarks for human health, and only 28 for aquatic life. Current standards and guidelines also do not account for mixtures of pesticide chemicals and seasonal pulses of high concentrations. Possible pesticide effects on reproductive, nervous, and immune systems, as well as chemically sensitive individuals, are not yet well understood. 6. Contaminant levels do not necessarily reflect the concentrations that humans will be exposed to in their drinking water supply, as nutrients and pesticides may be partially or completely removed through water treatment. 7. Although limited historical data are available to characterize long-term trends in surface water contaminants, this indicator specifically examines just the most current conditions.